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REARRANGEMENT OF ARYL SUBSTITUTED KETONES TO DIFLUORO SUBSTITUTED ETHERS IN ROOM-TEMPERATURE REACTIONS WITH XENON DIFLUORIDE

## B. Zajc and M. Zupan

Department of Chemistry and 'J. Stefan' Institute, University of Ljubljana, 61000 Liubljana (Yugoslavia)

Aryl substituted ketones are converted with xenon difluoride at room temperature to rearranged difluoro substituted ethers, while the reaction conditions, i.e. a catalytic amount of hydrogen fluoride, saturation of methylene chloride solution with hydrogen fluoride, or a hydrogen fluoride – pyridine mixture (70% hydrogen fluoride) as solvent, depend on the reactivity of the starting ketone, or the reactivity of the rearranged difluoro substituted ethers formed, where further fluorination of the aromatic ring can override the primary rearrangement process, yielding ring fluoro substituted rearranged difluoro ethers. In phenyl-alkyl substituted ketones, the phenyl group migrates, forming phenoxy derivatives, which are very reactive towards further fluorination; similarly, phenyl ring migration also occurs in reaction with 4-nitrophenyl phenyl ketone. Various benzocycloalkanones, e.g. 1-indanone, 1-tetralone, and 1-benzosuberone, are converted to 2,2-difluoro-3,4-dihydro-2H-1-benzopyran, or 2,2-difluoro-2,3,4,5-tetrahydro-1-benzoxepin, or 2,2-difluoro-3,4,5,6-tetrahydro-2H-1-benzoxocin derivatives, respectively.

$$Ar - C - R \xrightarrow{XeF_2} Ar - 0 - C - R$$

$$XeF_2 \longrightarrow F$$

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